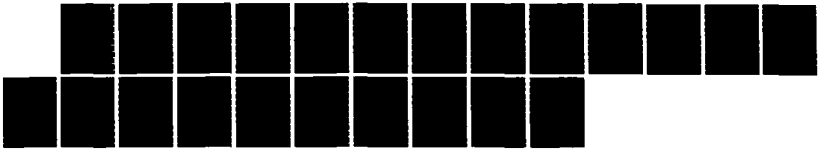
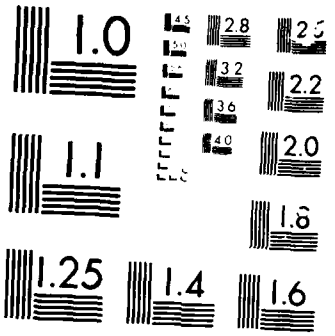
AD-A168 924 CALCULATED VERSUS EXPERIMENTAL CHARGE DENSITY DISTRIBUTION OF BE METAL(U) CORNELL UNIV ITHACA NY LAB OF ATOMIC AND SOLID STATE PHYSICS.. A J PINDOR ET AL. 1/1

UNCLASSIFIED JUN 86 TR-23 N00014-82-K-0576 F/G 20/8 NL




1.0
1.1
1.25
1.4
1.6
2.0
2.2
2.8
3.2
3.6
4.0

(12)

OFFICE OF NAVAL RESEARCH

Contract N00014-82-K-0576

TECHNICAL REPORT NO. 23

CALCULATED VS. EXPERIMENTAL CHARGE DENSITY DISTRIBUTION OF BE METAL

by

A.J. Pindor, S.H. Vosko and C.J. Unrigar

Prepared for Publication

in

Journal of Physics F

University of Toronto
Department of Physics
Toronto, Ontario
M5S 1A7, Canada

and

Laboratory of Atomic and Solid State Physics
Cornell University
Ithaca, New York 14853

June, 1986

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER: 23	2. GOVT ACCESSION NO. / 3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle): CALCULATED VS. EXPERIMENTAL CHARGE DENSITY DISTRIBUTION OF BE METAL	5. TYPE OF REPORT & PERIOD COVERED: Technical Report
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): A. J. Pindor and S. H. Vosko and C.J. Unrigar	8. CONTRACT OR GRANT NUMBER(s): N00014-82-K-0576
9. PERFORMING ORGANIZATION NAME AND ADDRESS: LASSP, Cornell University, Ithaca, NY 14853 Department of Physics, University of Toronto Toronto, Ontario, M5S 1A7, Canada	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS: Office of Naval Research 800 N. Quincy St. Arlington, VA 22217	12. REPORT DATE: June, 1986 13. NUMBER OF PAGES: 19
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report): unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

This document has been approved for public release and sale; its distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

Submitted for publication in Journal of Physics F

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

We have performed self-consistent Linearized Augmented Plane Wave calculations of the charge density of metallic beryllium, with and withlut warping of the interstitial potential, using the Local Density Approximation for the exchange and correlation energy functional. Overall agreement with the newest x-ray form factors is good, and it is argued that the remaining discrepencies have their source in the inadequacy of the Local Density Approximation and , for some reflections, in neglection the non-sphericity of the core charge density.

DD FORM 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-014-6601

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

CALCUALTED VS. EXPERIMENTAL CHARGE DENSITY DISTRIBUTION OF BE METAL

A.J.Pindor, S.H.Vosko

Department of Physics, University of Toronto,
Toronto,Ontario,M5S 1A7,Canada

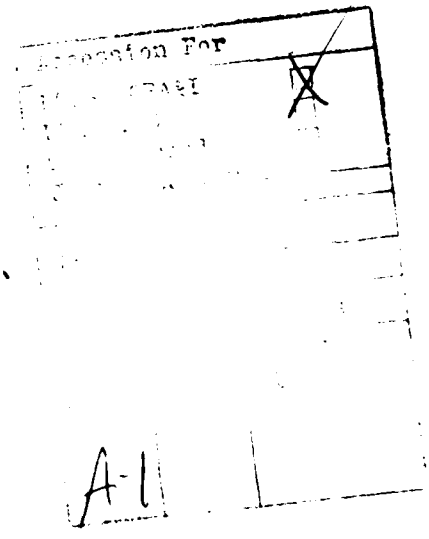
and

C.J.Umrigar

Laboratory of Atomic and Solid State Physics,
Cornell University, Ithaca, NY.14853, USA

Short title: Electronic charge density of Be metal

Classification number : 71.25P



A B S T R A C T

We have performed self-consistent Linearized Augmented Plane Wave calculations of the charge density of metallic beryllium, with and without warping of the interstitial potential, using the Local Density Approximation for the exchange and correlation energy functional. Overall agreement with the newest x-ray form factors is good, and it is argued that the remaining discrepancies have their source in the inadequacy of the Local Density Approximation and, for some reflections, in neglecting the non-sphericity of the core charge density.

1. INTRODUCTION

Recently very careful measurements of the X-ray structure factors for Be metal have become available (Hansen et al 1984). Since the X-ray structure factors are directly related to the electron charge density, which in principle is exactly calculable from Density Functional Theory (DFT), these results can be used as a stringent test of present day practice of DFT i.e. the Local Density Approximation (LDA) for the exchange and correlation energy funcional(for recent reviews see Theory of Inhomogenuous Electron Gas, ed.S.Lundqvist and N.H.March, Plenum Press, New York, 1983). In fact the X-ray structure factors provide a more severe test of LDA than its very successful application to the calculation of such physical quantities as cohesive energies, compressibilities, lattice constants etc., which are obtained from total energy differences where substantial cancellation of errors can occur (see Morruzzi et al. 1978). No such cancellation of errors takes place in the calculation of the structure factors.

It is important to be aware that in the practical implementation of DFT there are two distinct sources for the discrepances between theory and experiment. One, which may be termed as fundamental, is due to the fact that the exact exchange-correlation energy functional is unknown. As in

most current applications, the Local Density Approximation (LDA) (see eg. Williams and von Barth, 1983) is used in the present work (specifically the standard form for exchange with the Vosko et al. (1980),Hereafter referred to as VWN, form for the correlation part).The second comes from the computational aspect of the problem, namely the numerical solution of the self-consistent Kohn-Sham equations for the Belectrons in a crystal, for which a number of approximations must be made. Although in principle these are controllable, increasing the accuracy of the results puts rapidly growing demands on the necessary computer resources. In the present case we only require that the degree of self-consistency be such that the errors in the calculated form factors be less than the experimental ones.

To investigate the effects of the metallic environment on the charge redistribution in Be, we have performed Linearized Augmented Plane Wave (LAPW) calculations for the valence electrons,with and without warping of the interstitial potential. The 1s electrons were treated as atomic-like, since they had totally negligible amount of charge in the interstitial region (less than 0.001 of an electron). However, they were not frozen, i.e. their wave functions were recalculated at each iteration step.

We have used experimental lattice constants: a = 4.3211 and c = 6.7715 a.u. The resulting Fourier components of the charge density compare favourably with experimental data, as discussed below. However, a number of discrepancies remain. We argue, by reference to atomic LDA, Hartree-Fock (H-F) and Configuration Interaction (CI) charge densities, that the discrepancies for high Fourier components of the charge density are due to inadequacy of LDA to describe electron- electron interaction in the core region, where electron density gradients are large. We also expect that an appreciable discrepancy for the second Fourier component is due to the fact that we have not taken into account properly the distortion of the 1s core caused by the metallic environment.

2. OVERLAPPING ATOMIC CHARGE DENSITIES

As a first step we calculate the form factors for the density distribution corresponding to overlapping Be atomic electron densities obtained using different treatments of many-body effects. The intention is to calibrate the LDA with respect to more exact treatments (i.e. CI, which we consider virtually exact, and H-F), to have a reference system from which to measure metallization effects and

finally to have an estimate of the relative importance of core versus valence electron contributions to the form factors.

The results are summarized in Table I. The third column gives form factors obtained using atomic charge densities from a CI calculation using 55 configurations (Boyd 1979), the fourth column presents results from LDA, and the fifth - H-F calculation using Clementi and Roetti (1974) wave functions. For H-F results we also show separately the contribution from the 2s (valence) electrons. Finally column two shows the experimental results of Hansen et al.(1984), corrected for effects of atomic vibrations (Larsen et al 1980), together with estimated errors.

From a comparison of the three theoretical columns it can be seen that the H-F values are much closer to the "exact" CI values than the LDA ones. This is in agreement with previous observations that the local treatment of exchange is a more important source of error in the charge density than the neglect of correlation (Vosko and Wilk 1983). Moreover , the difference between H-F and CI is of the order or less than the experimental uncertainty, suggesting that if one could perform a calculation for the metal equivalent to H-F (e.g. essentially exact treatment of exchange within DFT) the error would be much smaller than

the experimental error and the main source of error would be in the accuracy of solving the Kohn-Sham equations..

Comparing CI and the experimental results for the individual wave vectors one sees that in most cases they differ by more than the uncertainity in the measurements indicating the necessity of including the effects of the crystal environment. On the other hand the magnitude of the differences generally decreases with increasing length of wave vector, as expected, since crystal field effects are smaller in the vicinity of the nucleus, which becomes more important as the order of reflection increases. However, since the LDA is used in the metallic calculation, it is also important to note that the magnitude of the percentage difference between the atomic CI and LDA calculations increases from ~ 0.5% to ~ 1% as the order of reflection increases. Thus we expect the difference in the LDA metallic calculation and experiment to increase with the magnitude of the wave vector. This is in fact what occurs as can be seen from Table II.

The other fact we would like to point out is that the contribution of the 2s states is only 1-2% of the total. Thus even though we expect the effect of the metallic environment on the core states to be small, it can have an appreciable influence on the change of form factors on

going from atom to metal, since the contribution from the core is the dominant part of the total form factor.

3. LAPW FORM FACTORS.

3.1 Calculational details

To study effects of metallization on the electronic charge distribution we have performed self-consistent, warped muffin-tin, LAPW band structure calculations (see e.g. Andersen 1975, Koelling and Arbman 1975), with the VWN form of LDA. Basis functions inside the muffin-tin included angular momentum components up to $\ell=8$ and in the interstitial region we found it necessary to go to over 50 plane waves, i.e. to take $k_{max} \cdot R_{MT} = 6.4$. Increasing $k_{max} \cdot R_{MT}$ to 7.5 did not modify the results in a significant way. The energy parameter was chosen in the middle of the band, E=0.4 Ry. Brillouin zone integrations were performed using the special points method (Fehlner and Vosko 1977), and we used as a standard 35 points in the irreducible part of the B.Z. Increasing this number to 57 had only a minor effect on the form factors. Nonsphericity of the valence charge density inside the muffin-tin was taken into account only approximately by analytically continuing the non-spherical part of the interstitial charge density into the

MT spheres. Since the non-sphericity is large only near the MT boundary this procedure yields a good approximation to the non-spherical part of the valence charge density. However this procedure cannot be used for the core charge density since so little of the core charge (less than 0.001 of an electron) is in the interstitial region that an analytic continuation would be unreliable. Hence we have not included the non-sphericity of the core charge. However the core charge was not frozen, i.e. the core wavefunctions were recalculated at each iteration step. The neglect of the small non-sphericity of the core charge is normally of no consequence but in the present calculation it is because no less than 96% of the form factors comes from the core charge and we are interested in the small changes in the form factors that occur on forming a solid. Hence we expect that possible discrepancies between our calculated form factors and the experimental ones will be due to the neglect of the core charge distortion and/or to inadequacy of LDA.

3.2 Results

Table II presents results of our calculations (warped and MT) and for comparison we also show results obtained by Ch[illegible] et al. (1983) using the self-consistent

pseudopotential method. The MT calculation was performed to investigate the importance of "warping" of the interstitial potential on the charge density. For the low order beams (with the exception of 002) the warped calculation agrees better with experiment than the atomic calculations. Warping is important for obtaining agreement for the lowest order reflection but affects the other reflections only slightly. The disagreement in the 002 form factor is probably due to our neglect of the non-sphericity of the core. Since the c/a ratio (1.57) for Be metal is appreciably different from that for an ideal hcp crystal (1.63) it is likely that the core charge would be more non-spherical than in a close-packed structure. The 002 component is sensitive only to distortions in the z direction.

Table III compares the form factors of the core charge density from our self-consistent calculations with those for a free Be atom using the VWN form of LDA. The difference between these form factors is shown in the fourth column and the difference divided by the corresponding geometric structure factor in the fifth column. The entries in the fifth column are all positive and increase with the magnitude of $\sin\Theta/\lambda$, indicating an expansion of the cores in the metallic environment as expected.

The values of the last three form factors obtained from the warped calculation are all appreciably smaller than the experimental values. This is probably due to the inadequacy of LDA when the gradients of the charge density are large.

The LDA is known to give much better results when used to calculate differences of various quantities than their absolute values. We can crudely include both the effects of metallization and non-local effects in the exchange correlation potential by recasting our results in terms of a difference in the two LDA calculations plus the CI form factor (using H-F atomic form factor, if CI was not available, would also be adequate):

$$f_D = f_{LDA}(met) - f_{LDA}(at) + f_{CI}(at) \qquad (1)$$

where $f_{LDA}(met)$ is our calculated form factor for the metal (column 2 of Table II), $f_{LDA}(at)$ is atomic form factor (column 4 of Table I) - both calculated within LDA and $f_{CI}(at)$ is the CI atomic form factor (column 3 of Table I). We see that in general we get an improvment, with the exception of the 002 reflection, which becomes worse. This again suggests that it is distortion of the cores due to the metallic environment, which is a source of the discrepancy in this case.

4. CONCLUSIONS

In conclusion we state that metallization effects are important for obtaining agreement of theoretical short wave vector Fourier components of charge density in metallic Be with recent accurate experimental data. In particular, for the shortest component inclusion of warping of the interstitial potential is essential. For higher q components the LDA seems to become less adequate, which is not surprising since such Fourier components are sensitive to the charge distribution in the core region where gradients of the charge density are large and hence corrections to LDA are expected to be substantial. We also note that the contribution from valence electrons constitutes less than 4% of the total value of the form factors (and this fraction goes down with increasing q) and hence even a small distortion of the core wave functions may contribute significantly to the form factors. We expect that this effect, not taken into account in our calculations, is responsible for marked disagreement between our calculated and experimental values for the 002 form factor.

5. ACKNOWLEDGMENTS

We thank Prof.R.J.Boyd for providing unpublished results of CI calculations.

This work was supported in part by a grant from the Natural Science and Engineering Council of Canada. CJU acknowledges the support of the Office of Naval Research.

REFERENCES

Andersen O K 1975 Phys Rev B12 3060-3070

Boyd R J 1979 private communication

Chou M Y Lam P K and Cohen M L 1983 Phys Rev B28 4179-4185

Clementi E and Roetti C 1974 At Data Nucl Data Tables 14 177

Fehlner W R and Vosko S H 1977 Can J Physics 55 2041-2058

Hansen N K and Schneider J R Larsen F K 1984 Phys Rev B29 917-926

Koelling D D and Arbman G O 1975 J Phys F: Metal Physics 5 2041-2054

Larsen F K Lehmann M S and Merisolo M 1980 Acta Crystal Sect A36 159

Moruzzi V L Janak J F Williams A R 1978 Calculated electronic properties of metals Perqamon Press Inc.

Vosko S H and Wilk L 1983 J Phys B: At Mol Phys 16 3687-3702

Vosko S H Wilk L and Nusair M 1980 Can J Phys 58 1200

Williams A R and von Barth U 1983 Theory of the Inhomoqenuous Electron Gas ed Lundqvist S and March N H Plenum Press New York pp 189-308

TABLE CAPTIONS

Table I

Form factors of overlapping atomic charge densities for Be, calculated within different approximations:
CI - Configuration interaction with 55 configurations (Boyd 1979;)
LDA - Local Density Approximation in VWN form (Vosko et al 1980);
H-F - Hartree-Fock using Clementi and Roetti (1974) wave functions;
H-F 2s (column 6) is the contribution from H-F ws wave function. Experimental data are from Hansen et al.(1984)

Table II

Form factors of charge density for metallic beryllium. Columns 2 and 3 show our LAPW results with (warped) and without (MT) warping of the interstitial potential. For comparison we also show the results of Chou et al.(1983) in

column 4. Experimental data are from Hansen et al.(1984). Column 6 gives the values of the quantity f_D defined in the eq. 1.

Table III

Structure factors of the core charge density for Be. The second column gives values obtained in our "warped" LAPW calculation, the third column refers to the LDA atomic calculation, the fourth column is the difference of the previous two and in the last one we give this difference divided by the geometric structure factor (GSF).

T A B L E I

hkl	Exp.	CI	LDA	H-F	H-F 2s
100	1.889(6)	1.826	1.817	1.818	0.020
002	3.432(7)	3.491	3.473	3.482	-0.034
101	2.938(7)	2.981	2.966	2.975	-0.044
102	1.550(11)	1.556	1.545	1.557	-0.036
110	2.909(18)	2.921	2.895	2.924	-0.036
103	2.406(12)	2.387	2.363	2.391	-0.006
200	1.368(7)	1.351	1.337	1.353	0.002
004	2.506(10)	2.527	2.497	2.531	0.024

T A B L E II

hkl	Present calc. warped	MT	Chou et al	Exp.	f_D
100	1.886	1.846	1.8845	1.889(6)	1.895
002	3.468	3.465	3.4418	3.432(7)	3.486
101	2.929	2.944	2.9255	2.938(7)	2.944
102	1.550	1.558	1.5365	1.550(11)	1.561
110	2.889	2.898	2.8669	2.909(18)	2.915
103	2.348	2.355	2.3362	2.406(12)	2.372
200	1.322	1.329	1.316	1.368(7)	1.336
004	2.470	2.478	2.4798	2.506(10)	2.500

T A B L E III

hkl	Metal ls	Atom ls	Atom-Metal	Atom-Metal/GSF
100	1.7873	1.7884	0.0011	0.0011
002	3.4901	3.4927	0.0026	0.0013
101	2.9955	2.9980	0.0025	0.0014
102	1.5729	1.5775	0.0022	0.0022
110	2.9142	2.9195	0.0053	0.0026
103	2.3524	2.3574	0.0050	0.0029
200	1.3273	1.3303	0.0030	0.0030
004	2.4541	2.4602	0.0061	0.0030

END

DTIC

7-86